



HAL
open science

Assessment of the ground spin state of iron(I) complexes: insights from DFT predictive models

Lidie Rousseau, Eric Brémond, Guillaume Lefèvre

► **To cite this version:**

Lidie Rousseau, Eric Brémond, Guillaume Lefèvre. Assessment of the ground spin state of iron(I) complexes: insights from DFT predictive models. *New Journal of Chemistry*, In press, 42, pp.7612-7616. 10.1039/C7NJ04816E . cea-01725248

HAL Id: cea-01725248

<https://cea.hal.science/cea-01725248>

Submitted on 7 Mar 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

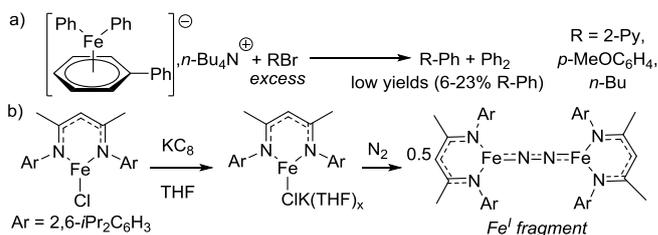
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Assessment of the ground spin state of iron(I) complexes: insights from DFT predictive models

L. Rousseau,^a E. Brémond,^b and G. Lefèvre*^a

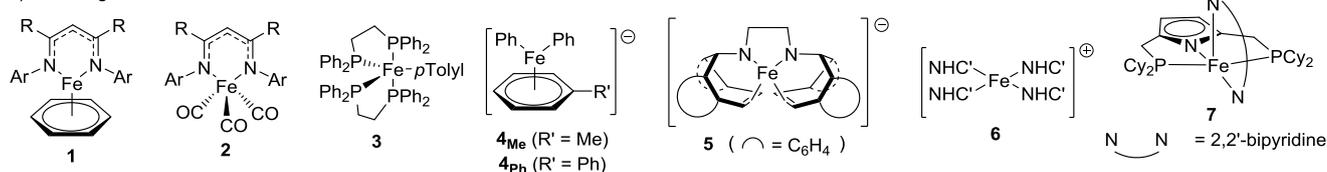
We propose an extensive DFT benchmark investigation dealing with the assessment of the ground spin state of various iron(I) organometallic complexes. Factors determining the spin multiplicity are discussed. A focus is put on the analysis of the electronic structure of bis-ligated X—[Fe^I—X species.

Over the last two decades, organoiron(I) chemistry has witnessed a rise of interest since the reactivity of such species is often discussed in diverse fields of molecular chemistry. Low-valent iron(I) complexes can indeed be obtained as intermediate species and/or off-cycle species in numerous stoichiometric or catalytic processes, such as Kochi-Kumada C—C bond formations¹ (Scheme 1a) or nitrogen activation (Scheme 1b).² A variety of well-defined iron(I) complexes has been synthesized and structurally characterized by X-Ray diffraction in the past. Stabilization of iron(I) oxidation state often requires strongly σ -donating ligands such as aryl groups,^{1,3,4} (silyl)amides,⁵⁻⁷ β -diketiminates,² or N-Heterocyclic Carbenes (NHCs).^{7,8} A full characterization of well-defined species can provide helpful data related to structural and electronic properties of the iron(I) oxidation state. Their ground electronic spin state S (doublet, $S = 1/2$, or quartet, $S = 3/2$) can moreover be unambiguously assessed using EPR and ⁵⁷Fe-Mössbauer spectroscopies. However, the characterization of transient and reactive iron(I) intermediates is a challenging issue. A representative example is the discussion of the putative role of iron(I) intermediates obtained as minor Fe-containing species in coligand-free Kochi-Kumada cross-couplings.⁹ The analysis of such cross-coupling reaction medium by EPR spectroscopy soon evidenced the presence of low-spin d⁷-iron(I).¹⁰ Yet, depending on the nature of the electrophile, iron(I) proved to be either unreactive or poorly active (Scheme 1a).¹ The instability of these intermediates also made difficult their characterization and thus the analysis of their reactivity. This issue led several groups to tentatively investigate the mechanistic aspects of Fe-catalyzed C—C cross-coupling reactions involving iron(I) intermediates by means of theoretical calculations, mostly by DFT methods.¹¹ In this context, gaining robust and viable predictive computational thermodynamic data for open-shell transition-metal-containing systems is not trivial. A common issue is the computational assessment of the electronic ground spin state of the metal (doublet or quartet for d⁷-iron(I)). Numerous DFT functionals tend to fail at this point. This is particularly true for low-spin species, since exchange-correlation functionals with a significant amount of exact-like exchange will strongly favor the high-spin configuration.¹² In a recent report, we showed that PBE0-D3, B3LYP-D3 and M06 associated with SDD or CEP-31G pseudopotentials for the metal did not reproduce the correct ground state for several iron(I) species experimentally characterized as low-spin.^{1a} However, B3LYP-D2 functional correctly predicted a doublet ground state for bis-diphosphino aryliron(I) complexes.¹³ Hu recently demonstrated that OPBE functional succeeded in the prediction of a doublet as a ground spin multiplicity for the complex $[(\eta^6\text{-PhPh})\text{Fe}(\text{Ph})_2]^-$ (Scheme 1a).^{1b} However, DFT analysis of the electronic structure of iron(I) complexes remains sporadic and no extensive benchmark of representative complexes has been reported so far.

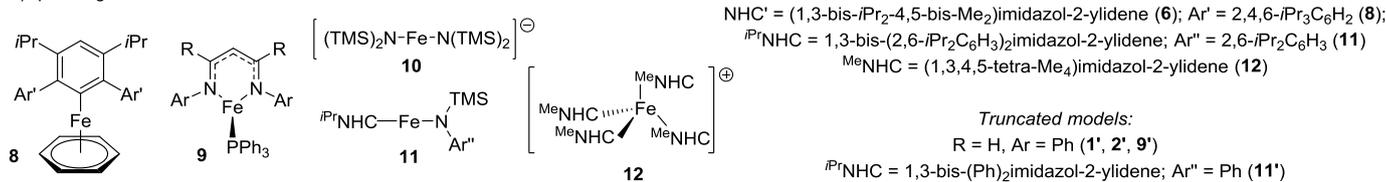


Scheme 1 Reactivity of iron(I) complexes towards organic electrophiles (a) and nitrogen (b).

a) doublet ground state:



b) quartet ground state:



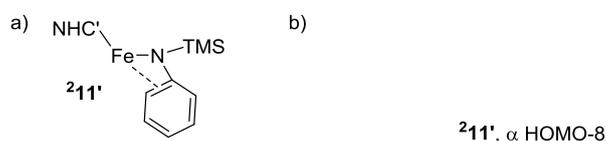
Scheme 2 Representation of the 12 iron(I) complexes benchmarked in this work; truncated models are labeled with a prime (e.g. **1'**).

Encouraged by Hu's results, we report a benchmark of ground spin state calculation for iron(I) mononuclear complexes using OPBE exchange-correlation functional, which combines the Handy's optimized exchange with the PBE correlation, and proved to correctly predict the ground spin state of numerous iron complexes.¹⁴

More precisely, we show that OPBE associated with the triple-zeta Ahlrichs' basis set (def2-TZVP) for the metal and 6-31G* for the main-group elements successfully reproduces the ground spin state multiplicity of a broad variety of iron(I) complexes. The nature of the electronic factors favoring the spin configuration are investigated. A focus is put on the analysis of the electronic structure of bis-ligated $[(\eta^n\text{-arene})\text{Fe}^{\text{I}}(\text{R})_2]^-$ species, and the role of the R-Fe-R angle and the arene coordination on the ground spin state are discussed. A set of 12 low- (Scheme 2a) and high-spin (Scheme 2b) complexes characterized in literature has been chosen, including β -diketiminate low-spin (**1**, **2**) and high-spin (**9**) species,² mono- (**3**^{4,13}, **8**³) and bis-aryl (**4**_{Me},^{1a} **4**_{Ph},^{1b}) species, bis-amido anionic complexes adopting a bent (**5**⁵) or a linear (**10**⁶) (N^-, N^-) geometry, bpy-stabilized species (**7**¹⁵), linear mixed NHC- and amido-stabilized species (**11**⁷), and tetracoordinated NHC cationic species in low-spin square planar (**6**) or tetrahedral high-spin (**12**) geometries.⁸ Table 1 gathers relative energies and Gibbs free enthalpies for both spin states, ground spin configuration ($S_{\text{G,c}}$), Fe Mulliken spin density (S_{Fe}), occupied d-block MOs energy span (calculated as the difference between the energies of the highest and lowest occupied d levels) and a comparison of the experimental (δ_{exp}) and calculated Mössbauer isomer shifts (δ_{calc}) when available.

These results show that OPBE allows the correct assessment of the ground spin state for all the benchmarked complexes. This is in stark contrast with the results obtained for functionals PBE0-D3, B3LYP-D3 and M06, which failed to predict the correct ground state for doublet complexes **1**, **4**_{Me} and **5**, and only assessed correctly the ground state of high-spin species such as **8** and **9**.^{1a} Relevant metric parameters of the first coordination sphere of the benchmarked complexes are reproduced *in silico* with a good accuracy, and no significant change in the computed doublet-quartet gaps was observed when using def2-TZVP basis set for all atoms for several benchmarked complexes (see SI), ensuring that smaller 6-31G* basis set for non-metallic atoms is a reliable choice. Except for **43**, computed spin densities on Fe are close to 1 (doublet) or 3 (quartet), in agreement with the characterization of complexes **1-12** as either pure doublet or quartet states, showing that no significant contamination from higher spin multiplicities occurred. Computation of the ⁵⁷Fe isomer shift of **23**, **24**_{Me}, **25**, **26**, **410**, **411** and **412** reflects the trend followed by the experimental values, with an average accuracy (absolute deviation ranking between 0.01 mm.s⁻¹ (**24**_{Me} and **25**) and 0.11 mm.s⁻¹ (**26**); see SI for the calibration curve).

The possibility of truncating bulky ligands is examined for β -diketiminate complexes **1**, **2**, and **9**, and for complex **11** (Scheme 2 and Table 1). The truncation has a strong effect on the compared electronic structures of **1/1'** and **9/9'**, since the doublet-quartet energy gaps significantly decreases in both cases, unlike to **2/2'** whose energy gap remained mostly unchanged (Table 1).¹⁶ The truncation of DIPP and ⁱPrNHC moieties in **11** allows a steric decompression in the optimization of **211'**, which shows an interaction between the metal ion and a C=C bond of the arylamine contrary to its experimental structure (Scheme 3a). Thus, the quartet-doublet span of the truncated pair **411'/211'** is much smaller compared to the non-truncated species **411/211**. Therefore, backbone truncation of the bulky ligands should be done carefully only once the exact spin state has been determined on a non-truncated model. It can also be drawn from Table 1 that complexes adopting a geometry leading to similar energetic d-spans for both doublet and quartet states follow the maximum electronic spin rule according to Hund's principle, accommodating a high-spin configuration. This is the case for complexes **8** (d-span: 0.73 eV for **28** and 1.07 eV for **48**, Table 1), **9** (1.07 eV for **29**, 1.28 eV for **49**), **11** (1.80 eV for **211**, 1.83 eV for **411**) and **12** (0.62 eV for **212**, 0.68 eV for **412**). The low-spin configuration will be favored by species featuring high-field ligands in their coordination sphere, e.g. the bis-diphosphino complex **3** (d-spans: 3.25 eV (**43**) vs 1.23 eV (**23**). **2** will similarly adopt a low-spin configuration (d-span: 2.77 eV for **42**, vs 2.39 eV for **22**), as well as **6** (d-span: 1.64 eV for **46**, vs 0.49 eV for **26**) and **7** (d-span: 2.66 eV for **47**, vs 1.11 eV for **27**).



Scheme 3 Metal-arene interaction in complex **211'** (a) and the associated bonding alpha MO (b).

Entry	G_Q-G_D E_Q-E_D (kcal.mol ⁻¹)		$S_{G,c}$	S_{Fe}	d-span (eV)	δ (mm.s ⁻¹)	
	exp.	calc.					
² 1	0.5	4.3	1/2	1.1	1.22	-	-
⁴ 1	5.7 ^[a]	8.8 ^[a]		3.1	2.56	-	-
² 2	30.9	35.4	1/2	0.9	2.39	-	-
⁴ 2	32.5 ^[a]	35.6 ^[a]		2.7	2.77	-	-
² 3	34.5 ^[b]	36.3 ^[b]	1/2	1.1 ^[b]	1.23 ^[b]	0.32	0.36
⁴ 3				2.4 ^[b]	3.25 ^[b]	-	-
² 4 _{Me}	22.8	25.6	1/2	1.2	0.92	0.28	0.27
⁴ 4 _{Me}				3.0	2.06	-	-
² 4 _{Ph}	24.1	27.1	1/2	1.3	0.87	-	-
⁴ 4 _{Ph}				3.0	2.14	-	-
² 5	15.4	17.5	1/2	1.2	1.09	0.20	0.19
⁴ 5				2.7	2.45	-	-
² 6	33.9 ^[b]	35.6 ^[b]	1/2	1.3	0.49	0.36	0.47
⁴ 6				3.0	1.64	-	-
² 7	3.2	3.5	1/2	1.3	1.11	-	-
⁴ 7				2.1 ^[c]	2.66	-	-
² 8	-8.5	-6.2	3/2	1.1	0.73	-	-
⁴ 8				3.1	1.07	-	-
² 9	-25.9	-24.3	3/2	1.2	1.07	-	-
⁴ 9				-34.7 ^[a]	32.9 ^[a]	3.1	1.28
² 10	-31.5	-30.9	3/2	1.0	0.97	-	-
⁴ 10				2.9	1.22	0.36	0.30
² 11	-27.4	-26.5	3/2	1.0	1.80	-	-
⁴ 11				-22.3 ^[a]	19.2 ^[a]	3.1	1.83
² 12	-27.6	-27.7	3/2	1.1	0.62	-	-
⁴ 12				3.1	0.68	0.57	0.49

Table 1 Computed data for complexes **1-12**. Spin multiplicities are superscripted. ^[a] values for the truncated complexes; ^[b] computed at the OPBE-D3(BJ) level; ^[c] $S_{bpy} = 1.0$.

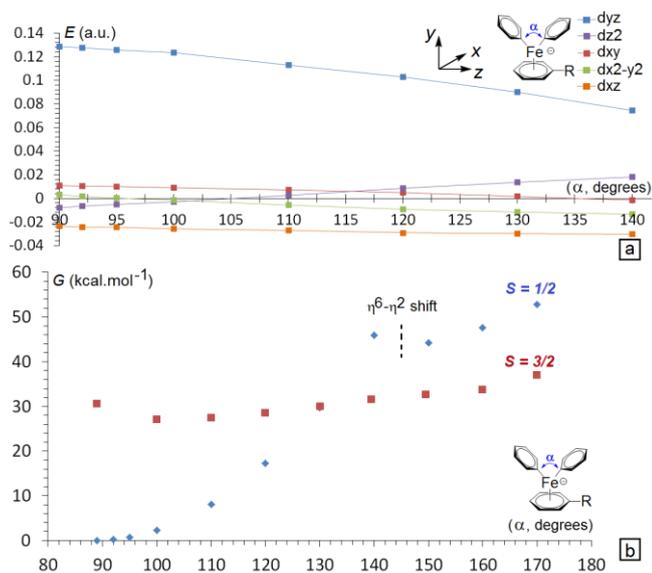
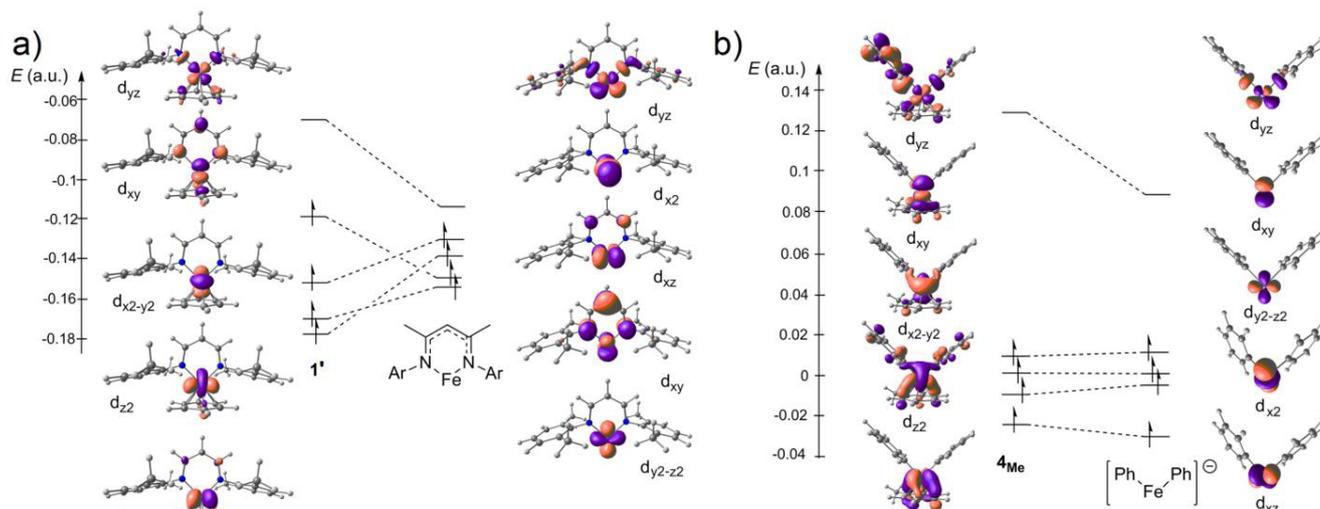


Fig. 1 Evolution as a function of the X-[Fe]-X angle (α) of the computed energies of the α d-MOs in ${}^2\mathbf{4}_{Me}$ (a), and of the relative energies of ${}^2\mathbf{4}_{Me}$ and ${}^4\mathbf{4}_{Me}$ (b).

For complexes with high coordination numbers or sterically bulky ligands such as **3** and **6**, correct structures and spin states are only obtained by adding the D3(BJ) classical dispersion correction to the OPBE functional.^{14d,e}

Optimization of **3** without dispersion corrections led to the decoordination of a PPh₂ ligand in the quartet state. The resulting tetracoordinated complex **43_{Td}** is found more stable than the pentacoordinated isomer **23** (see SI), contrary to the experimental structure of **3**. Similarly, no tetracoordinated structure is obtained for **46** without dispersion corrections. Electronic structures of **46/26** and **43/23** are therefore compared at the OPBE-D3(BJ) level (Table 1). This shows again that taking into account dispersion corrections is crucial to correctly reproduce the structure of systems involving bulky ligands.¹⁷ It is for instance demonstrated that London dispersion effects have decisive contributions in the stabilization of bulky NHC-ligated main-group species.^{17a}

Fig. 2 Evolution of the alpha d-MOs of **21'** (a) and **24_{Me}** (b) upon decoordination of the arene (C₆H₆ for **21'**, C₆H₅Me for **24_{Me}**; for beta MOs, see SI)



In the case of bis-ligated X—[Fe^I—X complexes (“X” = σ -donating ligand), two factors can have an influence on the ground spin state: the bending angle X—[Fe^I—X, and the presence (**1**, **4**) or the absence (**10**, **11**) of a η^6 -arene ligand to the metal. For d¹⁰ ML₂ complexes, a correlation between the presence of π -acceptor ligands and the L—[M]—L angle was reported by Bickelhaupt.¹⁸ For d⁷-Fe^I bis-ligated species, a first assumption is that bent complexes (X—[Fe^I—X = 92.9° (**21**), 88.6° (**24_{Me}**), 88.6° (**24_{Ph}**)) will adopt a doublet ground state, whereas linear complexes (X—[Fe^I—X = 179.3° (**410**), 173.4° (**411**)) will adopt a high-spin configuration. This is due to the antibonding interactions between the d_{yz} MO and the σ -donating ligands (C₆H₅[−] in **4**, β -diketiminato (N,N[−]) in **1**) in bent geometries. It leads to a destabilization of the d_{yz} level, thus increasing the ligand field, and favors a low-spin ground state. This tendency is reflected by the Walsh diagram of the alpha d-block MOs of **4_{Me}**: increasing the Ph—[Fe^I—Ph angle narrows the d-block span by stabilizing the d_{yz} level (Figure 1a). Accordingly, the quartet ground state becomes more stable for high bending angles (> 130°, Figure 1b). Optimized structures for complex **4_{Me}** leads to a η^4 -coordination mode of the arene. For bending angles higher than 150°, the steric pressure in **24_{Me}** leads to an arene hapticity shift to the η^2 coordination (Figure 1b). **1** also accommodates a low-spin ground state, due to antibonding interactions between the d_{yz} orbital and the β -diketiminato ligand. MOs analysis has been carried out on the truncated model **1'** (Fig. 2a). The overall energy span for the five d-MOs is smaller for complex **21'** (2.76 eV, Fig. 2a) than for complex **24_{Me}** (4.10 eV, Fig. 2b), although the bite angles of the β -diketiminato ligand in **21'** and the two C₆H₅[−] ligands in **24_{Me}** are close (X—[Fe^I—X: 91.8° in **21'**, 88.6° in **24_{Me}**), in agreement with the σ -donating effect of C₆H₅[−] in **4_{Me}**, stronger than the delocalized β -diketiminato in **1'**. However, computation of the spin states of model complex (**N,N[−]**)Fe (**1'** with no arene ligand) shows that a bent geometry is not a sufficient condition to favor a doublet ground spin state. **4(N,N[−])Fe** is indeed stabilized by 16.6 kcal.mol^{−1} vs **2(N,N[−])Fe**. This gap is smaller than for linear complexes **10** and **11**, which can be seen as a consequence of the bent coordination of ligand (N,N[−]) in (**N,N[−]**)Fe. The influence of the arene coordination on the spin state of bent complexes **1'** and **4_{Me}** has been investigated. Fragment decomposition analysis of the arene ligation on the alpha d-block MOs energies for **21'** and **24_{Me}** was performed. Figures 2a and 2b display alpha d-MOs evolution upon decoordination of the arene molecule on **21'** and **24_{Me}**. In both cases, the coordination of the arene leads to a destabilization of the d_{yz} level (0.04 a.u. for **21'**, 0.05 a.u. for **24_{Me}**), due to antibonding interaction of the latter with the arene 2 π MOs. This increases the ligand field, favoring the doublet configuration. Analysis of the beta MOs leads to similar observations (see SI). Adopting a low-spin state also leads to a vacant d-orbital on the iron(I), which can accept new ligands such as arenes (**1**, **4_{Me}**, **4_{Ph}**) or C=C bonds (**211'**, Scheme 3a).

We established that the OPBE functional (coupled with D3(BJ) classical dispersion correction for high-coordination numbers or bulky complexes) leads to a correct qualitative prediction of the ground spin state of a benchmark of iron(I) complexes. This level of theory allows us to show that the relative positions of the σ -donating ligands as well as the presence of arene/alkene ligands strongly contributes to the d-block MOs energy span, and therefore to the determination of the most stable spin multiplicity. Work is ongoing to compare our results to more quantitative quartet-doublet computed energy gaps obtained by modeling the corresponding electronic spectra at the same level of theory.

Conflicts of interest

The authors declare no conflict.

Acknowledgements

G.L. thanks the ANR JCJC program (project SIROCCO), as well as the CNRS, CEA and CINES (project sis6494) for their support.

Notes and references

- 1 (a) M. Clémancey, T. Cantat, G. Blondin, J.-M. Latour, P. Dorlet and G. Lefèvre, *Inorg. Chem.*, 2017, **56**, 3834-3848; (b) F. E. Zhurkin, M. D. Wodrich and X. Hu, *Organometallics*, 2017, **36**, 499-501.
- 2 J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela and P. L. Holland, *J. Am. Chem. Soc.*, 2006, **128**, 756-769.
- 3 C. Ni, B. D. Ellis, J. C. Fettinger, G. J. Long and P. P. Power, *Chem. Commun.*, 2008, 1014-1016.
- 4 C. J. Adams, R. B. Bedford, E. Carter, N. J. Gower, M. F. Haddow, J. N. Harvey, M. Huwe, M. Á. Cartes, S. M. Mansell, C. Mendoza, D. M. Murphy, E. C. Neeve, and J. Nunn, *J. Am. Chem. Soc.*, 2012, **134**, 10333-10336.
- 5 C. Lichtenberg, L. Viciu, M. Adelhardt, J. Sutter, K. Meyer, B. de Bruin and H. Grützmacher, *Angew. Chem. Int. Ed.*, 2015, **54**, 5766-5771.
- 6 C. G. Werncke, P. C. Bunting, C. Duhayon, J. R. Long, S. Bontemps and S. Sabo-Etienne, *Angew. Chem. Int. Ed.*, 2015, **54**, 245-248.
- 7 M. I. Lipschutz, T. Chantarojsiri, Y. Dong and T. D. Tilley, *J. Am. Chem. Soc.*, 2015, **137**, 6366-6372.
- 8 Z. Ouyang, Y. Meng, J. Cheng, J. Xiao, S. Gao and L. Deng, *Organometallics*, 2016, **35**, 1361-1367.
- 9 R. B. Bedford, *Acc. Chem. Res.*, 2015, **48**, 1485-1493.
- 10 (a) M. Guisán-Ceinos, F. Tato, E. Buñuel, P. Calle and D. J. Cárdenas, *Chem. Sci.*, 2013, **4**, 1098-1104; (b) G. Lefèvre and A. Jutand, *Chem. Eur. J.*, 2014, **20**, 4796-4805.
- 11 (a) A. Hedström, U. Bollmann, J. Bravidor and P.-O. Norrby, *Chemistry*, 2011, **17**, 11991-11993; (b) A. Bekhradnia and P.-O. Norrby, *Dalton Transactions*, 2015, **44**, 3959-3962.
- 12 M. Radoń, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14479-14488.
- 13 R. B. Bedford, P. B. Brenner, E. Carter, J. Clifton, P. M. Cogswell, N. J. Gower, M. F. Haddow, J. N. Harvey, J. A. Kehl, D. M. Murphy, E. C. Neeve, M. L. Neidig, J. Nunn, B. E. R. Snyder and J. Taylor, *Organometallics*, 2014, **33**, 5767-5780.
- 14 (a) M. Swart, A. W. Ehlers and K. Lammertsma, *Mol. Phys.*, 2004, **102**, 2467-2474; (b) M. Swart, A. R. Groenhof, A. W. Ehlers and K. Lammertsma, *J. Phys. Chem. A*, 2004, **108**, 5479-5483; (c) M. Swart, *J. Chem. Theory Comput.*, 2008, **4**, 2057-2066; (d) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (e) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
- 15 C. Vance Thompson, I. Davis, J. A. DeGayner, H. D. Arman and Z. J. Tonzetich, *Organometallics*, 2017, **36**, 4928-4935.
- 16 This might be due to the strong π -acceptor effect of the CO ligands, which overcomes the differences between the full β -diketiminato ligand and the truncated model.
- 17 (a) J. P. Wagner and P. R. Schreiner, *J. Chem. Theor. Comp.*, 2016, **12**, 231-237, (b) D. J. Liptrot and P. P. Power, *Nat. Rev. Chem.*, 2017, **1**, 0004 (review).
- 18 L. P. Wolters and F. M. Bickelhaupt, *ChemistryOpen*, 2013, **2**, 106-114.